

Synthesis and Characterization of Fe and FeS₂ (Pyrite) Catalyst Particles in Inverse Micelles*

A. Martino, J.P. Wilcoxon, A.P. Sylwester, J.S. Kawola
Fuel Science Division, 6211
Sandia National Laboratories
Albuquerque, NM 87185

Keywords: Inverse micelles; Nanophase clusters; Coal liquefaction catalysts

Introduction

Surfactant molecules possess two distinct moieties: a hydrophilic head group and a hydrophobic tail group. Because of the dual nature of surfactant molecules, they self-assemble in various solvents. In many two component systems of surfactant and oil, surfactants aggregate to form inverse micelles. Here, the hydrophilic head groups shield themselves by forming a polar core, and the hydrophobic tail groups are free to move about in the surrounding oleic phase. In three component microemulsion systems of water, oil, and surfactant, water is solubilized within the inverse micelle structure if the water concentration remains low. The solution takes on the structure of water droplets approximately 10-100Å in diameter dispersed in the oleic solvent with surfactant forming the boundary between the two components.

In structured solutions such as inverse micellar and oil-rich microemulsion solutions, polar chemical reactants can be compartmentalized in the interior of the surfactant aggregates. If a chemical reaction sequence is initiated, the surfactant interface provides a spatial constraint on the reaction volume. The surfactant aggregates act as micro-reactors. Metal alkoxide reactions [1], the formation of metal and semiconductor clusters [2-5], and the formation of polymer particles [6] are examples of chemical processes which have been carried out in structured surfactant solutions.

We have studied the formation of iron based clusters in inverse micelles and their use as catalysts in coal liquefaction reactions. Iron salts are solubilized within the polar interior of inverse micelles. The addition of an organic based reducing agent or water based sulfiding agent initiates respectively a chemical reduction or an exchange/replacement reaction. The inverse micelle structure acts as a reaction media and limits the final size of the particles. Particle formation is also dependent upon the particle nucleation and growth process. The initial micelle size, the nucleation and growth process, and ultimately the size of the particles is controlled by adjusting a few experimental parameters.

In order to illustrate the effects of various experimental conditions on the final particle size, we have studied a model system. CdS formation is well understood. We report the use of small angle neutron scattering, UV-visible spectrophotometry, and electron microscopy to characterize the inverse micelle solutions, the particle size, and particle elemental composition. Analogous results are observed in the formation of Fe and FeS₂ (pyrite). Finally, we report the use of the iron based clusters as catalysts in batch coal liquefaction reactions.

Experimental

Alkanes of increasing hydrophobicity from hexane to hexadecane, cyclohexane, and toluene were purchased from Aldrich at 99.9+% purity. Surfactants used included didodecyltrimethylammonium bromide (DDAB) from Kodak, butyl-ethylene glycol n-dodecyl ether (C₁₂E₄) from Nikkol, and POE (6) nonylphenol from Chem Services. Metal salts used included cadmium chloride, iron(II) chloride tetrahydrate, and iron(III) chloride hexahydrate from Aldrich. Lithium borohydride in tetrahydrofuran (1M) was purchased from Aldrich. Lithium sulfide was

* This work is supported by the U.S. Department of Energy at Sandia National Laboratories under contract DE-AC04-76DP00789.

purchased from Aldrich and prepared in a 1M solution in de-ionized, distilled water. Otherwise, all chemicals were used as delivered.

Stock solutions of 10 wt. % surfactant are prepared in various organic solvents to produce the inverse micelle solutions. The iron salts are added directly to prepare 0.001-0.01M solutions, and are mixed overnight on a stirring plate to assure complete solubilization. Concentrated aqueous cadmium chloride solutions are mixed with the stock inverse micelles solutions to prepare 0.0005-0.01M cadmium chloride microemulsions. To reduce the iron salts, the concentrated LiBH_4/THF solution is injected into the inverse micelle solutions under rapid stirring. To sulfide the iron and cadmium salts, the $\text{Li}_2\text{S}/\text{H}_2\text{O}$ solution is injected into the inverse micelle or microemulsion solutions under rapid stirring. The reaction is carried out and the final product is stored under dry, oxygen-free conditions. The reducing agent or sulfiding agent is added in an excess molar concentration to favor the formation of the surfactant stabilized sols.

The inverse micelle and cluster solutions are studied by small angle neutron scattering (SANS), UV-visible spectrophotometry, and electron microscopy (TEM). SANS is carried out at the Low-Q Diffractometer at the Los Alamos Neutron Scattering Center. Deuterated organic solvents are used. The inverse micelle radius of gyration is determined by Guinier analysis of the scattering curve [7]: $I = N \exp(-q^2 R_g^2/3)$, where N is a proportionality constant, q is the scattering vector, and R_g is the radius of gyration of the inverse micelles. UV-visible spectrophotometry of the particle solutions is completed *in-situ* with a Hewlett Packard 8452A diode array spectrophotometer. Relative size and characterization of the particles is achieved through analysis of the plasmon resonances observed in metal particles and the band gap structure observed in semiconductors. Finally, TEM using a Joel 1200EX sizes the particles and selected area electron diffraction aids in the particle characterization.

Coal liquefaction of DECS-17, Blind Canyon coal is completed in a stainless steel micro-batch reactor at 400°C, a cold H_2 pressure of 800 psi, and a reaction time of 30 minutes. Hexahydropyrene (H_6Py) is used as the hydrogen donor solvent. Thermal conditions are selected to give moderate conversion of coal to relatively low molecular weight organic material. Reaction analysis consists of extracting products with THF and heptane (C7) in two separate stages, and the products are separated into categories depending on their solubility for the solvents. Insoluble organic matter (IOM) is neither soluble in THF or C7. All soluble organic matter is extracted by THF (THF solubles), and the low molecular weight fraction of this material is extracted by C7 (C7 solubles). This latter fraction of product represents potentially usable oils and gases. Product gas analysis was not completed. A description of the coal liquefaction process is detailed elsewhere [8]. The iron based catalysts were tested *in-situ* or as powders and were added to the micro-batch reactors directly.

Results

Small angle neutron scattering results indicate that inverse micelles of C_{12}E_4 in octane and dodecane increase in size with the addition of water (Figure 1). The effect of water addition is more drastic in dodecane than in octane. Also, the inverse micelle size increases as the oil hydrophobicity increases (i.e. $\text{C}_{12}\text{E}_4/\text{dodecane}$ inverse micelles are roughly 12% bigger than $\text{C}_{12}\text{E}_4/\text{octane}$ inverse micelles).

Transmission electron microscopy of FeS_2 formed in $\text{C}_{12}\text{E}_3/\text{octane}$ inverse micelles show ~10Å radius particles (C_{12}E_3 is a slightly more hydrophilic analog of C_{12}E_4). Initial concentration of the iron salt was 0.001M. The particles show no signs of aggregation and are highly dispersed, spherical, and monodisperse on the TEM grid (Figure 2). TEM results indicate Fe^0 particles formed in DDAB/toluene (initial iron salt concentration = 0.001M) are ~12Å in radius. In addition, lattice fringe imaging indicates that the Fe^0 colloids exist in the high temperature fcc $\text{Fe}(\gamma)$ structure. Finally, CdS particles formed in $\text{C}_{12}\text{E}_3/\text{octane}$ inverse micelles (initial cadmium salt concentration = 0.0005M) are ~14Å in radius as determined by TEM.

The electronic spectra of CdS semiconductor particles is well known [3]. An absorbance shoulder is observed in the visible wavelength range due to the formation of an electron-hole pair across the semiconductor band gap. This spectra is reproduced by UV-visible spectrophotometry in

the CdS particles produced in inverse micelles (Figure 3). Increasing water concentration in the microemulsion solution causes a red shift in the onset of visible absorbance and a red shift in the absorbance maxima. The maxima occurs just before the large solvent absorbance shoulder. The electronic spectra is not effected by the solvent. The absorbance onset and maxima are nearly identical in octane and hexadecane.

The electronic spectra of FeS₂ particles is also dependent on water concentration in the microemulsion solutions (Figure 4). The spectra is highlighted by several absorbance maxima which red shift as the water concentration increases in the microemulsion mixtures. The behavior of the FeS₂ electron spectra is analogous to the behavior of the CdS electronic spectra as a function of water content.

As further characterization of the FeS₂ particles, electron diffraction from a selected area on the microscope grid produces a ring pattern consistent with the FeS₂ pyrite structure (Figure 5).

Finally, the Fe and FeS₂ particles were tested as catalysts in coal liquefaction reactions. Results are shown in Table 1. Solvent dispersed Fe or FeS₂ catalysts show equal or lower conversion to organic products compared to the thermal (no catalyst) reactions. The liquid catalysts show high amounts of insoluble organic matter. Fe catalyst added as a powder shows equal conversion to organic products compared to the thermal runs. FeS₂ catalyst added as a powder shows lower overall conversion to organic products, but a higher conversion to low molecular weight products. Importantly, the catalyst selectivity for the production of low molecular weight products is greatly increased.

Discussion

Colloid formation in the reduction and exchange/replacement processes proceed, respectively, via the following chemical reactions: $\text{Fe}^{2+} + 2\text{H}^+ \rightarrow \text{Fe}(\text{colloids}) + \text{H}_2$ and $\text{Fe}^{2+} + \text{S}_2^{2-} \rightarrow \text{FeS}_2(\text{colloids})$. The inverse micelles act as reaction vessels and mediate the nucleation and growth of the particles. The surfactant stabilizes the colloids and prevents flocculation and precipitation. Nevertheless, colloid stability is dependent on the high reactivity of the particles. It is necessary to use excess reactants in order to push the chemical reactions to the right and favor the formation of the colloids. In the case of the sulfiding reaction, water in the microemulsion mixtures favor the decomposition of the colloids into their respective ions. This is observed by the disappearance of the characteristic absorbance spectra of CdS and FeS₂. The presence of water in the reduction reaction of iron salts may change the chemistry all together and actually lead to the formation of iron borides and oxides. Oxidation of the iron clusters is visible to the naked eye, and CdS colloids photodegrade in the presence of oxygen ($\text{CdS} + 2\text{O}_2 \rightarrow \text{Cd}^{2+} + \text{SO}_4^{2-}$). The oxidation of both FeS₂ and CdS can be witnessed by the disappearance of their respective absorbance spectra.

Particle size control in the inverse micelle mediated synthesis of clusters is complex. It is reasonable to expect that the size of the initial inverse micelle will limit the final particle size. New particles will nucleate before existing particles grow large enough to disrupt the micelle structure. The nucleation and growth process is also governed by such variables as initial salt concentration, solution viscosity, and temperature. Any variable which increases the effective diffusion rate of the reacting ions will favor growth over nucleation and lead to larger particles.

We have attempted to elucidate the most relevant variables in the control of the final particle size. The electronic spectra of the semiconductor CdS provides us with the most facile method to determine relative particle size. The band gap of semiconductor particles increases with decreasing particle size due to quantum confinement of the charge carriers. Increasing particle size will cause a red shift in the absorbance spectra of fine particles [2]. The electronic spectra of CdS particles clearly show this behavior. Figure 1 shows that the size of inverse micelles is strongly dependent on water content and only weakly dependent on the hydrophobicity of the oil. The electronic spectra of particles synthesized in the same inverse micelles show a distinct red shift with increasing water content (Figure 3). There is little shift in the electronic spectra as the solvent changes from octane to hexadecane despite a six-fold change in solution viscosity. Clearly, the changing size of the initial inverse micelle plays a larger role in the final particle size than does ionic diffusion of reacting species as controlled by solution viscosity.

The electronic spectra of FeS_2 is dependent on the water content of the reacting microemulsion system (Figure 4). If we assume that the particles grow with increasing water content, then we can infer that the electronic spectra is size dependent for the FeS_2 particles. This is consistent with the formation of pyritic FeS_2 which is a semiconductor. The ring pattern of the selected area electron diffraction is consistent with the structure of pyritic FeS_2 and corroborates the electronic spectral data.

Iron sulfide has been studied extensively as a coal liquefaction catalyst. It is believed that pyrrhotite (Fe_{1-x}S) is the active form of the iron catalyst under liquefaction conditions [9], and that pyrite is reduced to pyrrhotite under liquefaction conditions [10]. We have attempted to use our Fe and FeS_2 (pyrite) particles as coal liquefaction catalysts. Wetting of Blind Canyon with our highly dispersed particle solutions causes coal aggregation and poor mixing. Aggregated coal which does not participate in the liquefaction process appears in the product as insoluble organic matter. Fe powder shows no improvement over thermal reactions perhaps indicating a need to sulfide the catalyst. FeS_2 (pyrite) powder however shows good selectivity towards the production of low molecular weight products at the same time that the insoluble organic matter content remained high. We infer that our catalyst shows high selectivity for reducing polar functionalities within Blind Canyon. Further studies of product quality are in progress.

Conclusions

Monodispersed, nanometer sized particles of Fe, FeS_2 (pyrite), and CdS are synthesized in inverse micelle solutions. Oil rich inverse micelle solutions are characterized by a structure in which surfactant interfaces protect a polar core from the oleic phase. Iron or cadmium salts are taken up in the polar core, and the clusters are formed upon chemical reduction or chemical exchange/replacement reactions. The inverse micelles provide size and geometric constraints on the growth of the clusters and stabilize the highly dispersed sols. The effect of initial micelle size as controlled by water content influences the final particle size more than solution viscosity which regulates the nucleation and growth of the particles. We have used the size dependent electronic spectra and selected area electron diffraction to characterize the formation of pyritic FeS_2 . Finally, the iron based clusters were tested as catalysts in a coal liquefaction process. While liquids wet the coal and prevent adequate mixing, FeS_2 powder selectively increases conversion to low molecular weight oils.

References

1. J.H. Jean and T.A. Ring, *Colloids and Surfaces*, **29**, 273, 1988.
2. M.L. Steigerwald and L.E. Brus, *Annu. Rev. Mater. Sci.*, **19**, 471, 1989.
3. B.H. Robinson, T.F. Towey, S. Zourab, A. Visser, and A. van Hoek, *Colloids and Surfaces* **61**, 175, 1991.
4. M. Boutonnet, J. Kizling, R. Touroude, G. Maire, and P. Stenius, *Catalysis Letters*, **9**, 347, 1991.
5. J.P. Wilcoxon and R.L. Williamson, *Mat. Res. Soc. Symp. Proc.*, **177**, 269, 1990.
6. L.M. Gan and C.H. Chew, *J. Dispersion Science and Technology*, **4**, 291, 1983.
7. G. Porod, *Small Angle X-ray Scattering*, Eds. O. Glatter and O. Kratky, pp. 24, Academic Press, 1983.
8. F.V. Stohl, Preprints of Papers Presented at the 205th ACS National Meeting, Denver, CO, 3/28-4/2/93, American Chemical Society, Division of Fuel Chemistry.
9. R.M. Davidson, *IEA Coal Research*, pp. 100, 1983.
10. T. Kotanigawa, S. Yokoyama, M. Yamamoto, and Y. Maekawa, *Fuel*, **66**, 1452, 1987.

TABLE 1. Micro-batch liquefaction results of Blind-Canyon, DECS-17 coal. Conditions: T = 400°C, P = 800 psi cold H₂, t = 30 min, hexahydropyrene solvent, 2-5 wt. % catalyst. Gas analysis is not included in these results.

CATALYST	% IOM	% THF SOLS/C7 INSOLS	% C7 SOLS
thermal, average	9.9	58.0	30.1
Fe, <i>in-situ</i>	66.5	13.8	8.9
Fe, powder	6.0	60.9	30.5
Fe, surfactant	50.0	27.3	22.7
extracted liquid			
FeS ₂ , <i>in-situ</i>	64.7	34.3	1.0
FeS ₂ , powder	17.0	33.9	44.4
FeS ₂ , surfactant	9.8	57.3	28.7
extracted liquid			

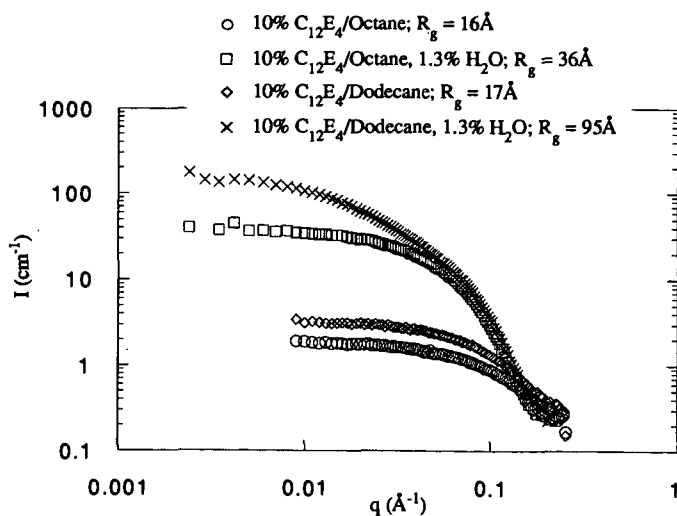


Figure 1. Small angle neutron scattering of inverse micelles. The inverse micelles grow as water concentration increases and as the oil alkane chain number increases.



Figure 2. TEM of FeS_2 (pyrite) clusters. The cluster radius is $\sim 10\text{\AA}$. The particles are highly dispersed and monodispersed. TEM's of Fe clusters show $\sim 12\text{\AA}$ radius particles and CdS clusters are $\sim 14\text{\AA}$ in radius.

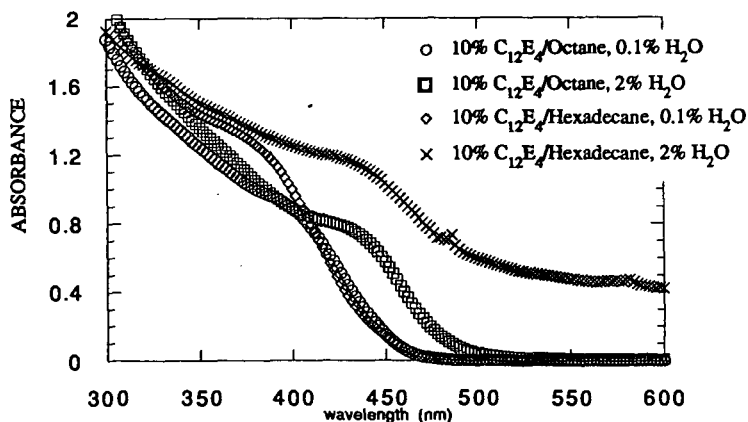


Figure 3. Electronic spectra of CdS clusters as a function of water content in two oil systems. As water content increases the absorbance maxima and onset red shift indicating an increase in the particle radius.

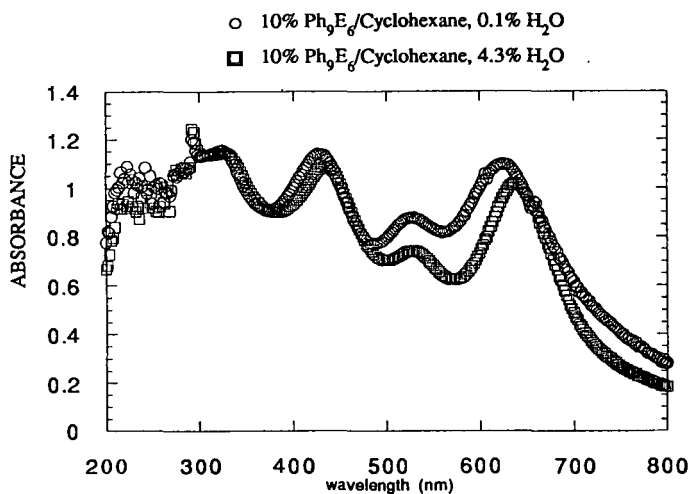


Figure 4. The electronic spectra of FeS_2 shows a red shift as water content increases. The size dependent band gap shift is characteristic of the semiconductor nature of pyrite.

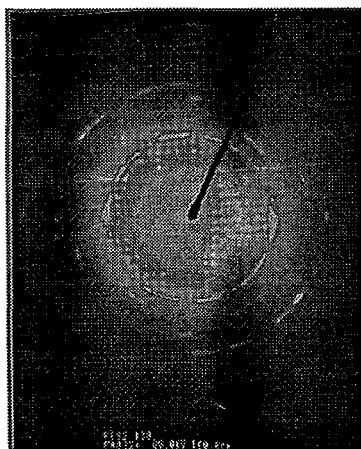


Figure 5. Selected area electron diffraction of FeS_2 shows a ring pattern consistent with the structure of pyrite.